III.A.19 Advanced Measurement and Modeling Techniques for Improved SOFC Cathodes

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Objectives

- Develop microelectrodes for improved isolation and measurement of the solid oxide fuel cell (SOFC) cathode overpotential (resistance) on cells having a thin electrolyte membrane.
- Develop nonlinear electrochemical impedance spectroscopy (NLEIS) for use in identifying what steps limit SOFC cathode performance.
- Generate a more detailed understanding of the electrochemistry governing SOFC cathodes, facilitating discovery and design of improved cathode materials and microstructures.

Approach

- Develop a MgO or MgO/spinel insulating mask layer which can regulate electrode/electrolyte contact with a spatial resolution of ±50 microns.
- Develop a powder-based synthetic route for porous single-phase perovskite electrodes of the lanthanum strontium cobalt ferrite (LSCF) family, such that for a given bonding temperature one can vary surface area, porosity, and electrode morphology.
- Fabricate thin-film LSCF electrodes on ceria electrolytes, varying A/B ratio, electrolyte dopant type and concentration, and La/Sr ratio.
- Measure current-voltage (*i-V)* characteristics, impedance, and NLEIS response for both thin-film and porous perovskite electrodes.
- Model cathode performance and NLEIS characteristics using finite element analysis (FEA) methods, applied to thin-film and porous microstructures.

Accomplishments

- Demonstrated the insulation properties of screen-printed MgO/spinel as an insulating, thermal-expansion-matched mask layer.
- Conducted microelectrode half-cell measurements on both Pt/ceria and lanthanum strontium cobaltite (LSC)/ceria, and showed that the half-cell *i-V* characteristics and impedance add correctly to predict the response of a symmetric cell made from the same materials.
- Demonstrated frequency isolation of microelectrode half-cells.
- Completed *i-V* characteristics, impedance, and NLEIS measurements of porous $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (LSC-82) electrodes (symmetric cells on Sm-doped ceria) in air, including 1st and 3rd harmonic data.
- Developed a *1-D* FEA model for the harmonic response of LSC-82 to third harmonic, as required to analyze the measured harmonics above.

- Discovered an anomalous negative 3rd harmonic response for LSC-82, which is inconsistent with existing models for oxygen reduction and bulk transport.

Future Directions

- Measure and model NLEIS response of symmetric cells of laser-deposited LSC electrodes.
- Measure and model NLEIS response of *half-cells* (1st, 2nd, 3rd harmonic) of porous LSC, and interpret using 1-D model which incorporates surface diffusion.
- Develop thinner, more spatially resolved mask for use on thinner electrolytes.
- Examine role of processing on LSC/ceria interfacial bonding and resistance, as distinct from catalytic properties and transport to the interface.

Introduction

Many promising new cathode materials for solid oxide fuel cells incorporate *mixed conducting ceramics* (materials which carry both oxygen ions and electrons) in order to substantially enhance oxygen reduction at reduced temperature[1]. For example, $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) cathodes utilize a significant portion of the electrode material surface, extending the reaction up to 10 microns from the electrode/electrolyte interface[2]. While these electrodes have proven promising in early exploratory research, they are only empirically understood[3], far from optimized[4,5], and can react unfavorably with the electrolyte[6,7]. Significant materials development is required to bring these electrodes to commercial fruition.

In order to address these issues, we believe a new generation of diagnostic tools are required that can accelerate the screening, fabrication, optimization, and long-term performance evaluation of cathode materials. One issue we are currently addressing is improved isolation and measurement of the cathode resistance as distinct from the rest of the cell. Commercially viable SOFCs require thin electrolytes (10-150 μm), making it difficult to separate anode and cathode resistances using standard cell tests. We are developing microelectrodes that potentially offer improved accuracy, faster throughput, and broader screening capabilities, while maintaining the ability to test cells made by commercially relevant fabrication methods. The second issue we are working on is new experimental methods for distinguishing what factors limit cathode performance. Although electrochemical impedance spectroscopy (EIS) is widely used for cathode development, results can be difficult to interpret in terms of mechanism and difficult to extrapolate to stack performance. We are currently developing extensions of EIS (NLEIS and electrochemical frequency modulation) that characterize the *nonlinear* cell response, potentially offering much higher resolution in terms of identifying rate-determining steps, separation of anode and cathode, and ability to predict cell performance based on half-cell measurements.

Approach

Figure 1 shows a schematic of the microelectrode cell design we are currently pursuing. The light area on the electrolyte surface is a mask

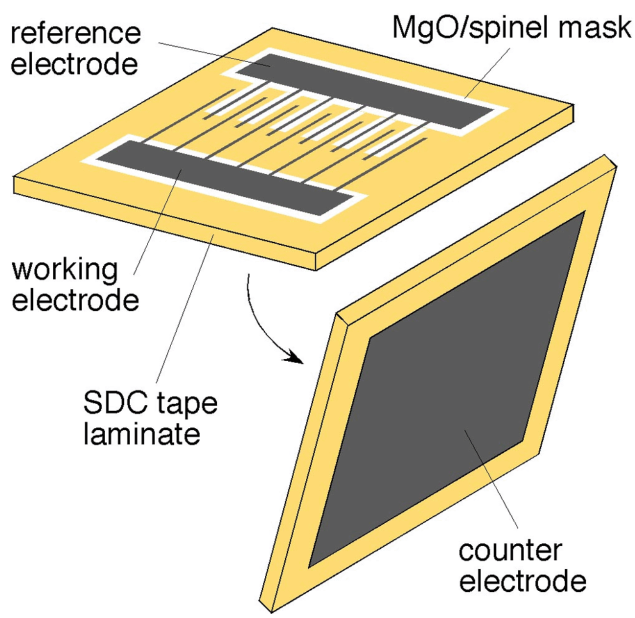

Figure 1. Cell Configuration of a Microelectrode Half-Cell

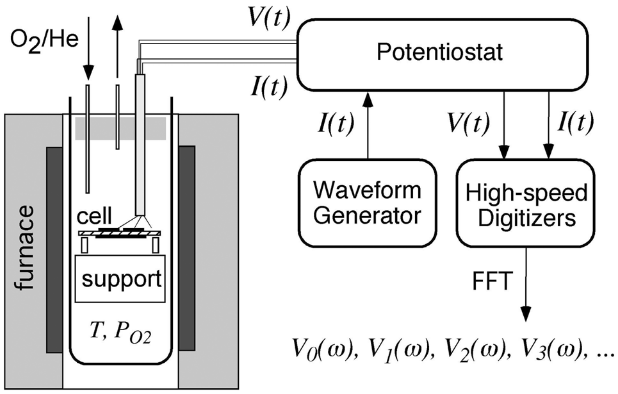

Figure 2. Schematic of NLEIS Experimental Apparatus

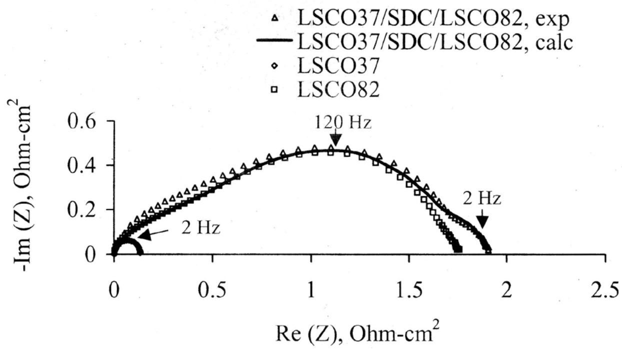

Figure 3. Impedance of LSC/SDC Cells in Air at 750°C

layer that regulates where the working and reference electrodes make contact to the electrolyte. In this way, the ohmic losses are well defined and confined to a region close to the working electrode (cathode) of experimental interest. Numerical simulations of this arrangement suggest that it provides a high degree of accuracy and frequency isolation. The mask layer is currently fabricated by screen printing and firing a MgO/spinel mixed powder ink onto a dense (fired) tape of Sm-doped ceria (SDC) electrolyte. The electrodes are subsequently processed onto the cell under the same conditions as any ordinary cell. Electrochemical measurements are then made, and performance is normalized to the actual area of the working electrode.

Figure 2 shows a schematic of our system for making NLEIS measurements. The frequency response analyzer normally used for impedance is replaced with a computer containing a sinusoidal signal generator and two synchronized high-speed analog-to-digital converters. The signal is used as the current set-point for a galvanostat, which measures and returns the current and voltage vs. time. These signals are then Fourier-transformed and analyzed to determine the magnitude and phase of any harmonics generated by the cell. These harmonics are analogous to those generated by a musical instrument around a base tone. One can tell which instrument is playing the same note (piano, oboe, violin) by the harmonics it generates. In our case, by constructing and solving physical models for the electrode's harmonic response, we can (in principle) tell which mechanism is correct by comparison of calculated and measured harmonics.

Results

Figure 3 shows the measured impedance of three cells. The first cell consists of a Sm-doped ceria (SDC) electrolyte, coated on one side with a full-sized (1 cm^2) porous $La_{0.3}Sr_{0.7}CoO_{3-\delta}$ (LSC-37) electrode, and on the other with a full-sized porous $La_{0.8}Sr_{0.2}CoO_{3-\delta}$ (LSC-82) electrode. The other two cells are microelectrode half-cells consisting of LSC-37 and LSC-82 working electrodes, respectively, on SDC. Both half-cells have a 1-cm^2 LSC-82 counterelectrode. With the exception of the mask layer, the microelectrode half-cells were processed identically to the cell with full-sized electrodes. Due to differences in composition and processing temperature, the LSC-37 and LSC-82 electrodes have very different characteristics; the impedance magnitude of the LSC-82 electrode is about 10 times larger than that of the LSC-37 electrode, and it has a characteristic frequency approximately 100 times higher.

As shown in Figure 3, the impedance of the LSC-37/SDC/LSC-82 cell consists of two arcs, which presumably represent contributions of the two electrodes, respectively. In contrast, the microelectrode half-cells show only one arc, which differ from each other in resistance and frequency response. After area normalization, the impedance of the two half-cells were added, yielding a "calculated" impedance spectrum for a LSC-37/SDC/LSC-82 cell, assuming the same ohmic membrane resistance as the actual cell. The data lie nearly on top of each other, which is a testament to both the accuracy and frequency isolation of the microelectrodes, as well as the reproducibility of fabrication in this case.

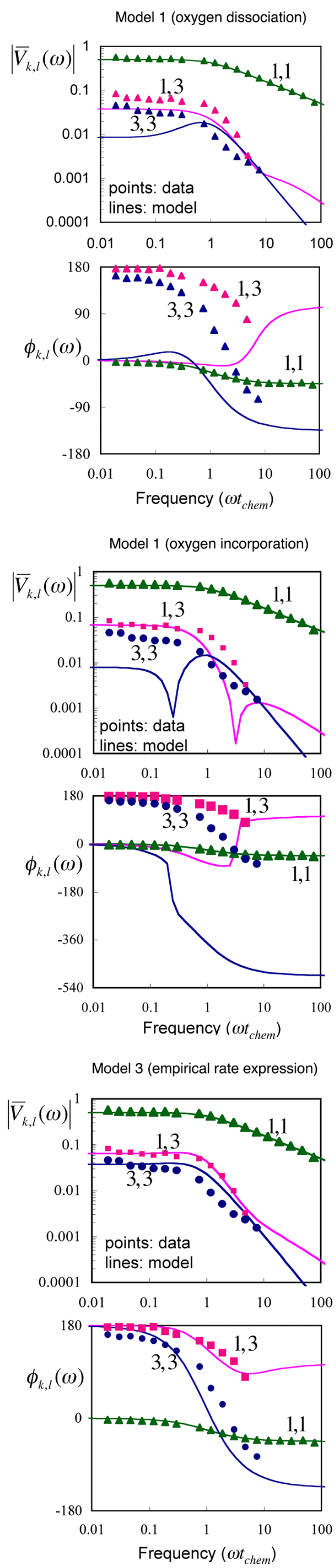

Figure 4. NLEIS Measurements of LSC-82/SDC at 750°C in Air

Moving on to NLEIS, Figure 4 shows Bode plots of the 1st (1,1) and 3rd (3,3) harmonic response of a symmetric LSC-82/SDC/LSC-82 cell in air at 750°C. Only the first and third harmonic signals are shown since the 2nd harmonic signal in this case was small due to the physical symmetry of the cell. Also shown is the 3rd-order contribution to the first harmonic (1,3), which can be thought of as a consistency check on the third harmonic. The data in the three columns are the same; the differences shown are various models for the response, which are explained below.

Figure 4 also shows calculated harmonics for the experimental results. All three models assume a bulk transport path for oxygen ions from the surface of the mixed conductor to the electrode/electrolyte interface, but make different assumptions about the mechanism of oxygen reduction. In the first model, oxygen reduction is assumed to be limited by oxygen dissociation. The second model assumes oxygen incorporation at the surface is limiting. Finally, the third column shows the predicted response assuming an empirical rate expression for oxygen reduction, which has never before been proposed.

The first thing to note is that all three of these models predict the same 1st harmonic (impedance). In other words, ordinary impedance (as a technique) does not provide any information that helps distinguish these various cases from each other. In contrast, the higher harmonics depend very strongly on the model assumptions. Clearly, model 1 (which is often assumed by workers) fails to predict many features of the data, even resulting in the wrong sign (180° phase difference) at low frequency. The second model is also wrong, predicting several nullifications (sign singularities) in the harmonic response, which are not observed. The best fit to the data appears to be model 3, but it is not yet clear if the improved fit is because the rate expression is correct, or merely because it is compensating for other false assumptions in the model (for example the neglecting of surface diffusion). We are currently investigating these issues.

Conclusions

Microelectrodes potentially offer an easy, low-cost way to isolate the performance of a particular electrode while maintaining the composition, microstructure, and processing of that electrode as closely as possible to the electrode of interest.

NLEIS is a potentially useful and powerful new technique which provides higher resolution than traditional linear impedance for distinguishing specific mechanisms governing electrode response.

FY 2004 Publications/Presentations

1. J.R. Wilson, D.T. Schwartz, and S.B. Adler, "Nonlinear Electrochemical Impedance Spectroscopy for Solid Oxide Fuel Cell Cathode Materials," *submitted to Electrochimica Acta*.
2. L.A. Dunyushkina, Y. Lu, and S.B. Adler, "Microelectrode Array for Isolating Electrode Polarization in Planar SOFC's," *in Preparation*.

Special Recognitions & Awards/Patents Issued

1. Charles W. Tobias Young Investigator Award of the Electrochemical Society (2004).

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